Determination of Chlorides in Tobacco

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Two potentiometric titration procedures, one a manual and the other an automatic titration method, were tested for the determination of water-soluble chlorides in tobacco. Thirteen laboratories tested the manual procedure on six tobacco samples and obtained good intra- and interlaboratory precisions. Only five laboratories were equipped to perform the automatic titration procedure and, even though no two laboratories used the same apparatus, the precision was very good. The manual procedure is being recommended for adoption as official, first action.

A rapid potentiometric titration procedure (1, 2) for determining chlorides in tobacco was subjected to collaborative testing. Thirteen laboratories participated in the study; each laboratory analyzed six samples in duplicate. The samples included one each of Burley and Flue-cured stems, and Burley, Flue-cured, Maryland, and Wisconsin leaf.

A second study was also made in which an automatic titrator was required. However, only five laboratories participated and of these, only one used the titrator recommended.

METHODS

Method I (Manual Procedure)

Reagent

Silver nitrate soln.—0.1*N*. Stdze against KCl as in sample analysis.

Table 1. Collaborative results on the determination of chlorides in tobacco by Method I

Coll. No.	Sample Number[a]						Std Dev., %	pH Meter Used
	1	2	3	4	5	6		
1	1.86	1.93	0.62	0.66	0.35	1.10	0.011	Beckman
2	1.87	1.94	0.61	0.67	0.36	1.10	0.009	Fisher Titrimeter
4	1.90	1.96	0.64	0.68	0.35	1.12	0.000	Electronic Instruments, Ltd.
5	1.90	1.95	0.62	0.67	0.35	1.11	0.015	Beckman GS
8	1.90	1.94	0.63	0.67	0.34	1.10	0.007	Fisher Titrimeter
9	1.94	1.98	0.65	0.73	0.43	1.16	0.009	Sargent Recorder
11	1.87	1.93	0.62	0.68	0.35	1.10	0.004	Precision Shell
12	1.86	1.92	0.64	0.67	0.35	1.11	0.003	Beckman H–2
13	1.90	1.96	0.63	0.68	0.35	1.13	0.003	Leeds and Northrup
15	1.84	1.88	0.60	0.64	0.33	1.08	0.006	Fisher Titrimeter
22	1.86	1.92	0.60	0.66	0.33	1.08	0.005	Electronic Instruments, Ltd.
23	1.88	1.92	0.63	0.67	0.34	1.10	0.005	Beckman H–2
24	1.87	1.87	0.61	0.59	0.34	1.06	0.015	Fisher Titrimeter
$\bar{\bar{X}}$	1.88	1.93	0.62	0.67	0.35	1.10		
s	0.026	0.031	0.017	0.031	0.025	0.025		

[a] 1, Burley stems; 2, Flue-cured stems; 3, Burley leaf; 4, Flue-cured leaf; 5, Maryland leaf; 6, Wisconsin leaf.

Apparatus

(a) *pH meter.*—Leeds and Northrup, Beckman, or equiv., equipped with Ag and glass electrodes, Beckman Nos. 1261 and 1190-42, resp., or equiv.

(b) *Buret.*—10 ml, graduated in 0.05 or 0.02 ml, preferably reservoir type.

Determination

Weigh accurately ca 2 g tobacco, ground to pass No. 40 sieve, into 250 ml electrolytic beaker. Add 100 ml H_2O, small amount at first to thoroly wet tobacco, then remainder. Let stand at least 5 min. at room temp., stirring intermittently. Pipet 5 ml HNO_3 (1 + 9) into mixt. and insert clean electrodes. Start magnetic stirrer and continue stirring thruout titrn at rate sufficient to produce vigorous agitation without spattering. Titr. with std 0.1*N* $AgNO_3$ soln to potential previously established as equivalence point. Det. equivalence point potential graphically by making several titrns on one or more tobacco samples. Recheck occasionally, and redet. when either electrode is replaced. Record vol. of titrant and calc. % Cl = ml $AgNO_3$ × Normality × 3.5453/g sample.

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Method II (Automatic Titration Procedure)

Reagent

Use same reagent as in Method I, above.

Apparatus

(a) *Automatic titrator.*—Sargent-Malmstadt, E. H. Sargent and Company No. S-29690, equipped with platinum or platinum-rhodium indicator and calomel reference electrodes.

(b) *Buret.*—Same as for Method I, above.

Determination

Proceed as in Method I through ". . . stirring intermittently." Add 7.5 ml HNO_3 (1 + 9) to mixt. Adjust flow rate of automatic titrator so that 9–10 ml $AgNO_3$/min. is delivered from buret. Position beaker under electrodes, close buret stopcock, press automatic button, and when an audible "click" is heard, open buret stopcock. (If instrument cuts off after addn of few drops titrant, close buret stopcock, press automatic switch, and when click is again heard, reopen stopcock.) Stirrer and valve shut off automatically at end point. Read buret, record vol. titrant, and press manual button to allow 2–3 drops titrant to flow thru tip. Rinse electrodes and tip; then proceed with next titrn.

Calc. % Cl as in Method I.

Table 2. Collaborative results on the determination of chlorides in tobacco by Method II

Coll. No.	Sample Number[a] 1	2	3	4	5	6	Std Dev., %	Automatic Titrator Used
2	1.91	2.02	0.65	0.71	0.37	1.13	0.000	Sargent Spectrophotometric-Electrometric Model SE
5	1.87	1.91	0.63	0.68	0.36	1.11	0.006	Sargent Model A Dual Recording Titrator
8	1.92	1.95	0.62	0.68	0.35	1.12	0.005	Fisher Titrimeter
13	1.90	1.93	0.63	0.69	0.37	1.13	0.004	Sargent-Malmstadt
22	1.88	1.94	0.63	0.67	0.33	1.10	0.006	Electronic Instruments, Ltd.
$\bar{\bar{X}}$	1.90	1.95	0.63	0.69	0.36	1.12		
s	0.021	0.042	0.011	0.016	0.017	0.013		

[a] See Footnote in Table 1.

Results and Discussion

Method I

Thirteen collaborators analyzed the six samples in duplicate and reported all values. The data shown in Table 1 are the average values to the nearest 0.01% for each collaborator and each sample. Within-laboratory standard deviations calculated from the difference between duplicates are shown, as well as the interlaboratory standard deviations for each sample. Both the inter- and intralaboratory precisions are excellent, the former varying from 0.017 to 0.031%, the latter from 0.000 to 0.015%.

Method II

Only five collaborators used automatic titration equipment in this study and only one used the instrument specified. The mean values for each sample from each laboratory are shown in Table 2 together with the inter- and intralaboratory standard deviations. Although five different automatic titrators were used, the interlaboratory precisions were very good and within-laboratory precisions were all excellent. It is obvious, however, that there is too much diversity in the apparatus used to standardize on any one automatic apparatus. Although automatic titrators may be used and are undoubtedly more rapid, they are not essential since Method I, the manual procedure, is quite satisfactory particularly when a line-operated pH meter is used.

Recommendation

It is recommended that Method I for determining chlorides in tobacco be adopted as official, first action.

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R. S. Wade, Imperial Tobacco Co.

These data were also presented as a committee report to the Tobacco Chemists' Research Conference, Sept. 26–28, 1962, at Richmond, Va.

REFERENCES

(1) Harrell, T. G., Abstracts of Papers, Eighth Tobacco Chemists' Research Conference, November 11–12, 1954, Richmond, Va.
(2) Nelson, R. A., *This Journal,* **43**, 518 (1960).

The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee A, and was adopted by the Association. See *This Journal*, **46**, 99 (1963).

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